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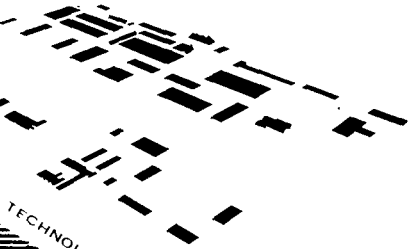
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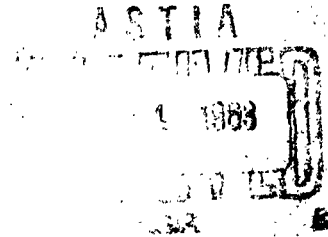
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Report No. ARF-1208-12A  
(Final Report)

UNCOOLED IR DETECTOR  
FOR THE TEN MICRON REGION

Chief, Bureau of Naval Weapons

Report No. ARF-1208-12A  
(Final Report)

UNCOOLED IR DETECTOR FOR THE TEN MICRON REGION

March 1, 1962 through February 28, 1963

Contract NOw 62-0751-c  
ARF Project 1208

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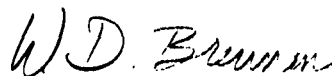
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## FOREWORD

This Final Report describes the research performed under Contract NOW 62-0751-c from 1 March 1962 to 28 February 1963. The research objective of this project is the development of an uncooled infrared detector for the 10 micron region. The principle of operation of the proposed detector is the modulation of exciton-induced photoconductivity by the infrared energy. Principal contributors to the research described in this report are W. D. Brennan, project leader, J. Kroll, and S. Webb. Data are recorded in logbooks 12415, 12567, 12569, 12632, 12804, 12805, 12808, 12824, 13102 and 13185.

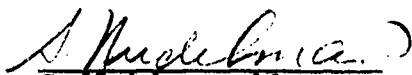
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## ABSTRACT

### UNCOOLED IR DETECTOR FOR THE TEN MICRON REGION

This report summarizes the experimental effort carried out under Contract NOW 62-0751-c for the Bureau of Weapons during the period 1 March, 1962 to 28 February, 1963. The objective of this research program is to develop an uncooled infrared detector for the  $8\mu$  to  $12\mu$  atmospheric window. In contrast to all other quantum infrared detectors, the principle of operation of the proposed detector does not involve free carrier generation by the infrared radiation. Instead, the detector shall use the absorption of infrared energy by excitons to quench an exciton-induced photoconductivity.

In this report methods and techniques to observe exciton-induced photoconductivity and quenching by infrared radiation are discussed. During the course of the work some 90 crystals were examined, and while the quenching effect was never observed, 11 of these crystals appear to exhibit the required exciton processes.

The experimental procedures are being modified to emphasize the observation of exciton transport and to remove some interferences that might have inhibited or masked the quenching in previous experiments.

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## UNCOOLED IR DETECTOR FOR THE TEN MICRON REGION

### I. INTRODUCTION

This final report describes the results of research to explore the feasibility of using exciton absorption of infrared energy to develop a useful uncooled detector for the ten micron region. This work was done under Contract NOw 62-0751-c; this report covers the period March 1, 1962 to February 28, 1963 and represents the combined reports for that interval.

Diemer noticed that exciton-induced photoconductivity in CdS could be quenched by illuminating the crystal simultaneously with infrared light with any wavelength from  $0.8\mu$  to  $10\mu$ . Apparently the infrared energy ionized the excitons before they reached the contact region. Unless the free electron-hole pairs are formed near the contacts, they cannot contribute to the photoconductivity. This is due to the holes being trapped almost immediately, producing internal electric fields which prevent electrons from reaching the contacts. Only one of Diemer's twenty-five crystals exhibited this strong exciton diffusion and quenching phenomena. Subsequent work in these laboratories by R. J. Robinson confirmed the observation of infrared quenching of exciton-induced photoconductivity; Robinson observed the effect in one crystal out of seven selected for examination.

The experiments described above supplied the motivation for the present research. The objective of this effort under Bureau of Weapons sponsorship is to exploit this phenomena of infrared quenching to develop a useful uncooled detector for the  $10\mu$  region. The entire effort during this report period was directed toward discovering crystals in which exciton-induced photoconductivity could be quenched by radiation in the  $10\mu$  region.

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Despite the fact that approximately 90 crystals of CdS were examined during this period, many of them by several methods, the infrared quenching phenomena was never observed although in eleven of these crystals excitons are suspected of contributing to the photoconductivity. There is no reliable explanation for this adverse development; the optimistic view is that we are victims of statistics.

## II. EXCITONS IN CADMIUM SULFIDE

An exciton is an electron and a hole in a crystal bound together through their mutual electrostatic attraction and rotating about their common center of mass. The configuration of an exciton, then, is similar to that of a hydrogen atom, except that the electron and proton in a hydrogen atom exist in empty space where the dielectric constant is unity while the exciton moves in a material of high dielectric constant. It can be shown that the ionization energy of a hydrogen atom is inversely proportional to the square of the dielectric constant,<sup>2</sup> so one would expect that the ionization energy of an exciton (equivalent to the distance below the conduction band of the exciton ground state) in a typical semiconductor to be of the order of  $10^{-2}$  times the ionization energy of hydrogen. In cadmium sulfide early spectrographic measurements in which a regular absorption series (analogous to the fundamental series in hydrogen) was observed near the absorption edge suggested an exciton ionization energy of about 0.1 ev. Later measurements<sup>3</sup> suggest a lower figure, about 0.03 ev. Considering that the macroscopic dielectric constant of CdS<sup>4</sup> is about 9.3 and the ionization energy of hydrogen is 13.5 ev, the exciton ionization energy is in order-of-magnitude agreement with the hydrogenic approximation.

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It is apparent that an exciton is free to move through a crystal lattice and is unaffected by electric fields since its net charge is zero (except that a sufficiently high electric field can dissociate the exciton through a process similar to field emission). The exciton can be dissociated into a free hole and electron thermally or by absorbing a photon of energy greater than its ionization energy. For the two ionization energies mentioned above, 0.1 ev and 0.3 ev, the corresponding photon wavelength is  $12.4\mu$  and  $41\mu$ .

Although theoretically an exciton can move through a crystal and considerable experimental evidence has been amassed which supports the mobility of excitons, considerable controversy exists over whether excitons actually are as mobile as some of the experiments indicate. The papers by Diemer and his co-workers<sup>1</sup> present strong evidence that photoconductivity observed between two contacts on crystalline CdS which are well removed from the illuminated region, can be partly due to the diffusion of exciton produced in the illuminated region. These excitons diffuse through the crystal to the region near the contacts where they are ionized thermally. In their papers the authors carefully consider the contribution which scattered light and fluorescence radiation can make to the photoconductivity; the only apparent conclusion is that excitons can be important in this long-range photoconductivity. Specifically, they conclude that the diffusion length of excitons can be several millimeters and their lifetime nearly  $100\mu$  sec. Diemer's work has been vigorously, although unconvincingly, attacked.<sup>5</sup> The opponents to the exciton transport theory have never explained all of Diemer's results with any non-exciton hypothesis.

It is interesting to note that long-range photoconductivity similar to that described above has been observed in germanium.<sup>6</sup> During a discussion

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of this work (which was reported orally), it was suggested that the photoconductivity should be quenched by illuminating the crystal with infrared radiation.<sup>7</sup>

### III. EXPERIMENTAL

At the outset of the program the plan of research included efforts to select crystals of CdS which exhibited the long-wavelength infrared quenching effect, but the primary research effort was to be an evaluation of the use of this effect in a practical detector. Instead of following this plan, the actual research effort was almost totally a search for the quenching effect. An outline of the experimental effort is given below while the work is discussed in detail in Appendix I.

The apparatus used in most of the experiments consisted of a visible light source which could be focussed on the crystal of CdS a known distance away from the contacts. Various light sources (incandescent, mercury-xenon arc, and monochromatized) and optical systems (including one which incorporated a 14" f/0.5 mirror for high light collecting efficiency) have been used in our attempts to generate excitons in CdS. The source of infrared energy was a Nernst glower whose output was filtered by a wafer of InSb. The crystal is mounted in a sample holder which is designed so that the visible light falls on a fixed slit behind which the crystal can be positioned by means of a micrometer screw adjustment. The infrared energy is incident on the opposite face of the crystal.

First attempts to observe quenching consisted simply of measuring the photocurrent due to visible light with and without infrared incident on the crystal. This work was done using monochromatized light and white light.

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No reproducible change in the photocurrent due to the infrared was observed in some 40 crystals examined by this method.

The sensitivity of this dc detection system was quite adequate to observe quenching of the magnitude observed by other workers (for example, R. J. Robinson observed a quenching which amounted to several percent). In an attempt to improve the sensitivity, the system was modified by chopping the infrared and using a tuned amplifier as a signal detector. Again, no quenching was observed in 10 crystals using this method.

At this point in the program the progress had been disappointing. We felt that more positive results could be obtained by searching for evidence of exciton transport, which is a necessary prerequisite for the desired quenching effect to exist. The technique used in these measurements consisted of chopping the visible light and observing the photoconductive rise curve on an oscilloscope. The shape of the rise curve will depend on the mechanism responsible for producing photoconductivity. The particular shape of the curve expected to result from exciton diffusion is derived in Appendix II and plotted on page 21. Using this technique we planned to select those crystals in which exciton processes are important.

Nearly 50 crystals were examined in the search for exciton transport. Most of the photoconductive rise curves of these crystals could be ascribed to scattered light reaching the contact region, but 11 showed evidence of another mechanism. The rise curves of these 11 crystals do not match the curve shape expected from exciton diffusion. We do not yet understand this different photoconductivity mechanism, but work in progress at this time is designed to yield more information about these processes.

Some crystals were examined at 77°K by the methods discussed

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above. It is recognized that exciton processes are enhanced at lower temperatures through an increase in the exciton lifetime. Some crystals did show greater evidence of the photoconductive mechanism previously seen in the 11 crystals mentioned above, but still no quenching effects were observed.

Details of the experimental work outlined above are contained in Appendix I.

#### IV. SUMMARY

The experimental work done on this program has been described. The effort has primarily been a search for crystals of CdS in which exciton induced photoconductivity can be quenched by infrared radiation in the band from  $8\mu$  to  $12\mu$ . Some 90 crystals have been examined, and while the quenching has not been observed, a suggestion of an exciton contribution to the photoconductivity has been observed in eleven crystals. We do not yet possess a detailed understanding of the photoconductive behaviour of these eleven crystals. Thus one cannot be positive that exciton processes are important in these crystals; these uncertainties provide the motivation for work in the immediate future.

The most singular feature of this work is that the desired quenching effect was never observed even though it had been observed previously by two other people, R. J. Robinson at ARF and Diemer at Philips Research Laboratory. Unfortunately, the crystals measured by Robinson were ground and sintered, and could not be re-examined. Since Robinson's crystals were originally grown in this laboratory, it may be necessary in any future work to grow new crystals again. This adverse development has forced a re-orientation of the program away from an Edisonian search for suitable crystals

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and toward a more fundamental study of exciton transport.

The primary aim of future efforts will, of course, continue to be to obtain semiconductor crystals in which the photoconductivity can be quenched by 8-12 $\mu$  infrared radiation. The direction of the work will be oriented more closely to the study of exciton generation and transport than in the past, however, for we now feel that only in this way can significant progress be made.

Several questions have been raised by the work described in this report. The unexplained non-linearities in the photoconductive rise curves of some crystals should be investigated further. If, as is suspected, these curves are actually due to exciton diffusion, why are their shapes so markedly different from the expected curve shape? If, as suggested above, the exciton contribution vanishes after several exciton lifetimes, what is the mechanism for attenuation of the exciton flux? And, if we are seeing exciton diffusion, why can we not modulate this current with infrared? These questions must certainly be answered before a detector of the type proposed is optimized.

To this end, the most promising crystals already studied will be re-examined in an arrangement similar to that previously used to study the rise curves. The light pulses, however, will be very short to ensure that exciton decay is not caused by the generating source. This technique should clearly display any exciton contribution to the photoconductivity. The exciton contribution will occur after the light has been turned off and the photocurrent essentially constant. This work will be done at room temperature and at lower temperatures, ranging down to 77°K. Furthermore, the temperature dependence of conductivity will be examined carefully to ensure that exciton properties will be distinguished from any thermal effects.

Materials preparations procedures used to obtain the crystal measured

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by Robinson will be re-examined. Crystals will be prepared if this study indicates new materials rather than improved measurements techniques are required.

The theoretical aspects of exciton generation and transport will be re-examined by Dr. S. S. Mitra. A fundamental program is in progress and under his direction for understanding lattice dynamics of a crystal through determination of optically active lattice modes. The finer details in the reststrahlen or lattice absorption spectra arises from the interaction of optical modes with the phonons characterizing the elastic vibrations. The importance of the phonon distribution in the understanding of a host of solid state properties, like heat capacity, thermal and electrical conductance, thermal expansion, intensity of x-ray reflection etc., is well known. Dr. Mitra will investigate the known properties of excitations, and try to arrive at some understanding of the way in which they might interact with the basic crystalline properties noted above. In this way, a realistic, fundamental approach will be carried out for the purpose of developing an uncooled long wavelength (8-12 $\mu$ ) infrared detector. Dr. Mitras' interest and experience in optical properties of solids makes him particularly well qualified to carry out this study.



## APPENDIX I

### THE SEARCH FOR QUENCHING OF EXCITON-INDUCED PHOTOCONDUCTIVITY IN CdS

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## APPENDIX I

### THE SEARCH FOR QUENCHING OF EXCITON-INDUCED PHOTOCONDUCTIVITY IN CdS

#### I. Early Experimental Arrangements and Results

The initial experimental facility used a monochromater for spectral selection of light to generate excitons, while infrared radiation was obtained from a Nernst glower, filtered with a 0.005 inch InSb single crystal wafer. The InSb absorption edge is at approximately  $6.5\mu$ , and its transmittance for wavelengths longer than  $6.5\mu$  is approximately 30%. For some experiments a germanium wafer, 1 mm thick, was used as an IR filter. This crystal's absorption edge is near  $1.7\mu$  and its transmittance for longer wavelengths is 55%.

The use of a monochromater as a visible light source was dictated by the expectation that the efficiency of exciton production would be wavelength dependant. The data-taking procedure initially consisted of focussing the line of visible light at various distances up to several millimeters from the contacts and measuring the photoconductive response of the crystal while the wavelength of the incident light is varied from 400 to 700 m $\mu$ . Then the infrared energy is allowed to fall on the crystal and the photoconductive response is remeasured. The photocurrents measured in this way are subtracted and plotted as a function of wavelength. Figure 1 shows the sample configuration during these measurements; for pictorial clarity the visible and infrared light is shown incident on the same crystal face, while in practice these two beams were incident on opposite faces. Typical results of these first experiments are shown in Figure 2 where the ordinate is the

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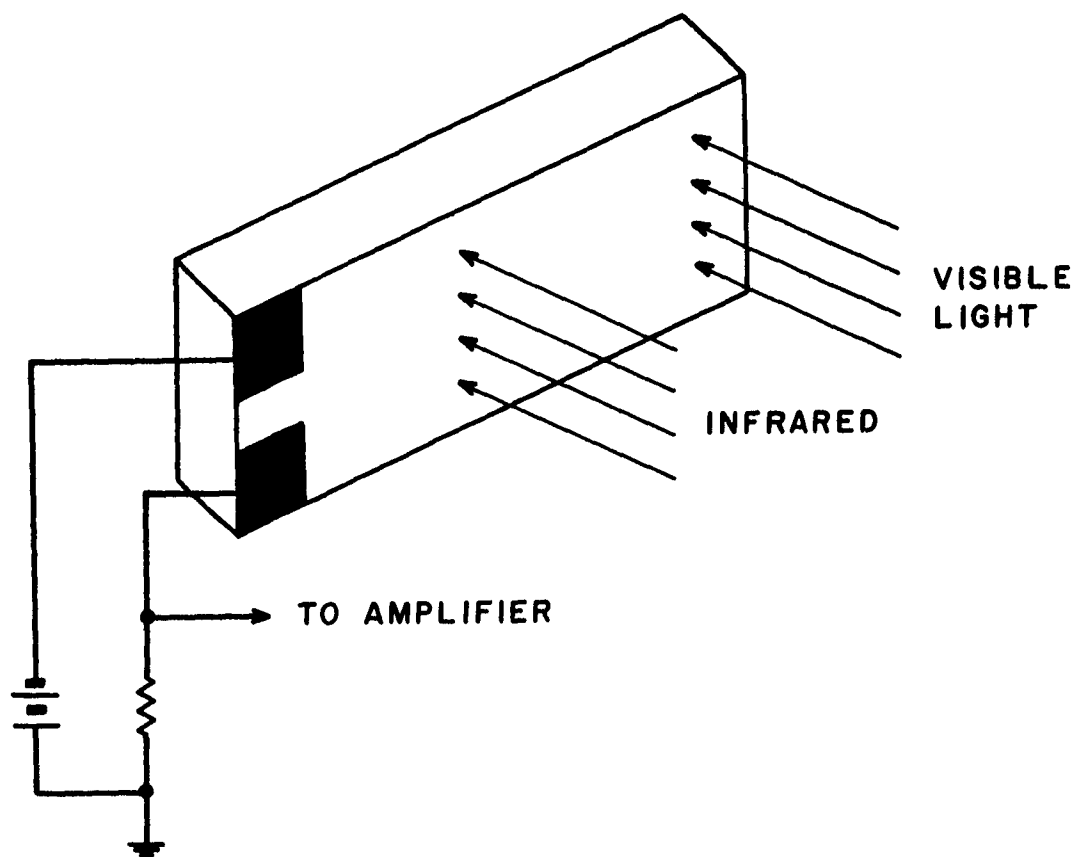


FIG. 1 SAMPLE CONFIGURATION

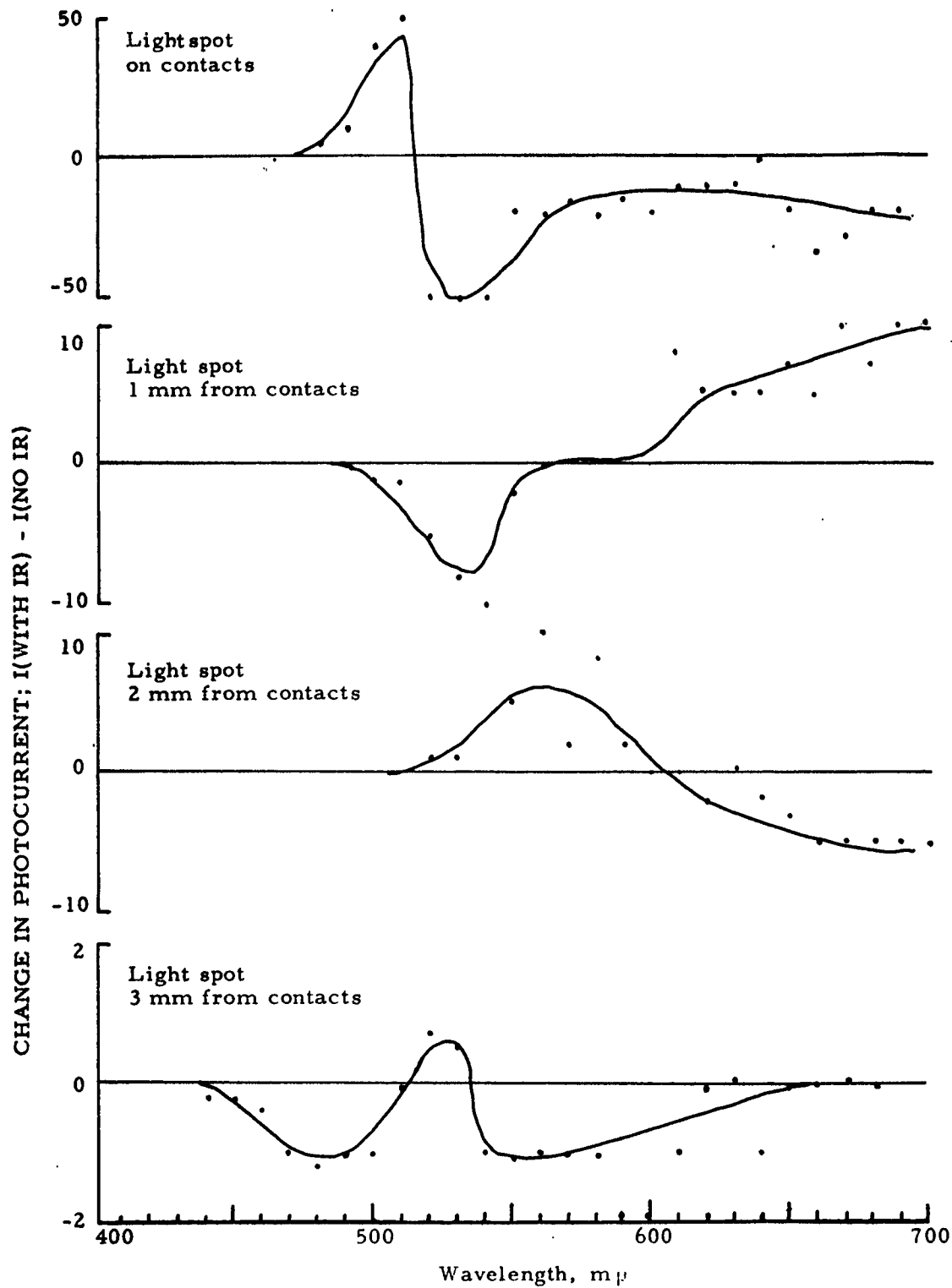


Fig. 2 - APPARENT EFFECT OF IR ON PHOTOCURRENT - SAMPLE Y-2

change in photocurrent due to the infrared. While a quenching seems to occur at 540 mμ when the light spot is within 1 mm of the contacts, these results were not reproducible and probably resulted from fluctuations in the intensity of the monochromator beam. The light source used for the monochromator was powered from the a. c. line, and even though a Sola transformer was used to regulate the line voltage, the regulation was not perfect.

The method of measurement was then changed so that the photocurrent was measured with and without infrared incident on the crystal for each wavelength before proceeding to the next monochromator setting. This procedure eliminated erratic results due to long term drift and fluctuations. These measurements were far more reproducible, and indicated that the infrared radiation caused no modulation of the photocurrent in some 25 crystals.

It is recognized that one of the factors determining the sensitivity of exciton-induced photoconductivity to quenching by infrared is certainly the rate of exciton production by visible light. In an effort to increase the rate of exciton production the incandescent lamp source for the monochromator was replaced by a mercury-xenon high pressure arc lamp, and finally the monochromator itself was replaced by a 550 mμ interference filter. The center wavelength and band width of the light passed by this filter could be adjusted to shorter wavelengths by tilting the filter.

The measuring instrument in all the work thus far discussed was a Keithley 150-A Microvolt-Ammeter. In addition to being a very sensitive instrument, this meter can be used in a suppressed-zero mode; in this mode the meter applies a bucking voltage to the incoming signal so that the meter indication is the difference between the incoming signal and the bucking voltage. With the meter then operating at a higher sensitivity the minimum detectable change in signal level is about 0.01%. Despite this excellent instrumentation,

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no change in signal level was ever noted upon application of the infrared energy, even with the increased illumination brought about by the changes in the optics noted above.

## II. Detection Sensitivity and an A. C. Detection System

The sensitivity of the D. C. type of measurements discussed above is far greater than that used by either Diemer and his co-workers or Robinson. In terms of Specific Sensitivity, defined as

$$S_1 = \frac{V}{JE} \left[ \frac{(R_c + R_1)^2}{4R_c R_1} \right],$$

where  $V$  = rms value of signal in volts

$J$  = rms value of radiant energy flux in watts/cm<sup>2</sup>

$R_c$  = zero signal detector resistance

$R_1$  = load resistance

$E$  = bias applied across detector and load resistor in volts

we estimate our maximum sensitivity to be about 1 cm<sup>2</sup>/watt. For comparison, the specific sensitivity of lead sulfide detectors at 25°C varies from 10 to 1000 cm<sup>2</sup>/watt while  $S_1$  for lead selenide detectors at 25°C varies from 0.2 to 2 cm<sup>2</sup>/watt. Actually our minimum  $S_1$  varies somewhat from sample to sample depending on the magnitude of various noise sources, but 1 cm<sup>2</sup>/watt is a typical figure. Thus we can report that  $S_1$  for these specimens of CdS is at least 10 to 1000 times less than that of lead sulfide, but could be comparable to that of lead selenide at 25°C. These estimates are based on thermopile measurements of the incident infrared energy, a known battery voltage and measurable load resistance. The infrared energy transmitted by the InSb filter is 320 μ watts/cm<sup>2</sup> at the sample location, while

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that transmitted by the germanium filter is  $3350\mu$  watts/cm<sup>2</sup>.

In an effort to increase the sensitivity of our signal detection, the incoming infrared was chopped and a harmonic wave analyzer (tuned amplifier) was used to search for a signal. The sensitivity of this arrangement surpassed that of the previous dc measurements. About 20 crystals were examined for photoconductive quenching with this ac detection system, and no response to infrared was noted in any crystal.

At this point in the program, some 49 crystals had been examined to determine whether they exhibited the desired quenching of the photoconductivity by infrared energy in the 8-12 micron band. Many of these crystals were examined by several of the techniques and arrangements described above, yet no evidence of the quenching effect has been observed. It should perhaps be noted that quenching could nearly always be observed with unfiltered light from the Nernst glower and occasionally with the germanium filter in the path of the infrared beam, but never when the indium antimonide filter was in place. This quenching is not the effect we are seeking, but rather is caused by absorption of infrared energy of wavelength less than about  $1.75\mu$  by trapped holes, thus hastening the recombination of photo-excited electrons and holes<sup>8</sup>. The utilization of this process in a detector is futile because the effect is limited to wavelengths less than  $1.75\mu$  and the response time constant is of the order of 1 second.

### III. The Search for Exciton Diffusion

In view of the fact that no quenching by long wavelength infrared was observed in any of the relatively large number of crystals described above, we decided that a new approach to the problem might be more profitable. It

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will be recalled that the essence of the proposed detector is that excitons are generated by visible light and that their lifetime should be long enough so that they may diffuse a considerable distance through the crystal. The new approach is a more definitive search for crystals in which exciton processes are observable on the premise that these processes may be more observable than the quenching effect. Those crystals in which exciton processes are important to the photoconductivity should be those in which modulation of the photocurrent by long-wavelength infrared will be most likely.

In these experiments the usual line of visible light, in which the infrared is filtered out, is focussed on the crystal several millimeters from the contacts. The light is chopped and the shape of the rise curve of the photoconductivity is observed on an oscilloscope. The experimental arrangement is shown in Figure 3. The sample holder and micrometer screw adjustment for positioning the line of visible light are more clearly shown in Figure 4. In Figure 3, the visible light source is in the rectangular box at the right; the image of the filament is focussed in the plane of the chopper, and is then collimated and refocussed on the sample. A small part of the collimated beam is reflected to a phototube which supplies the trigger for the oscilloscope. The Nernst glower is contained in the black box at the left.

If only the initial part of the rise curve is observed such that the period of observation of the rise curve of the photoconductivity is much less than the carrier lifetime then, to a first approximation, we may neglect free carrier recombination. In our experiments the total observation time never exceeded 1 millisecond, while the carrier lifetime is about 15 milliseconds. The observed photocurrent in this situation can be due to several causes: (a) scattering of the direct illumination by multiple reflections leading to

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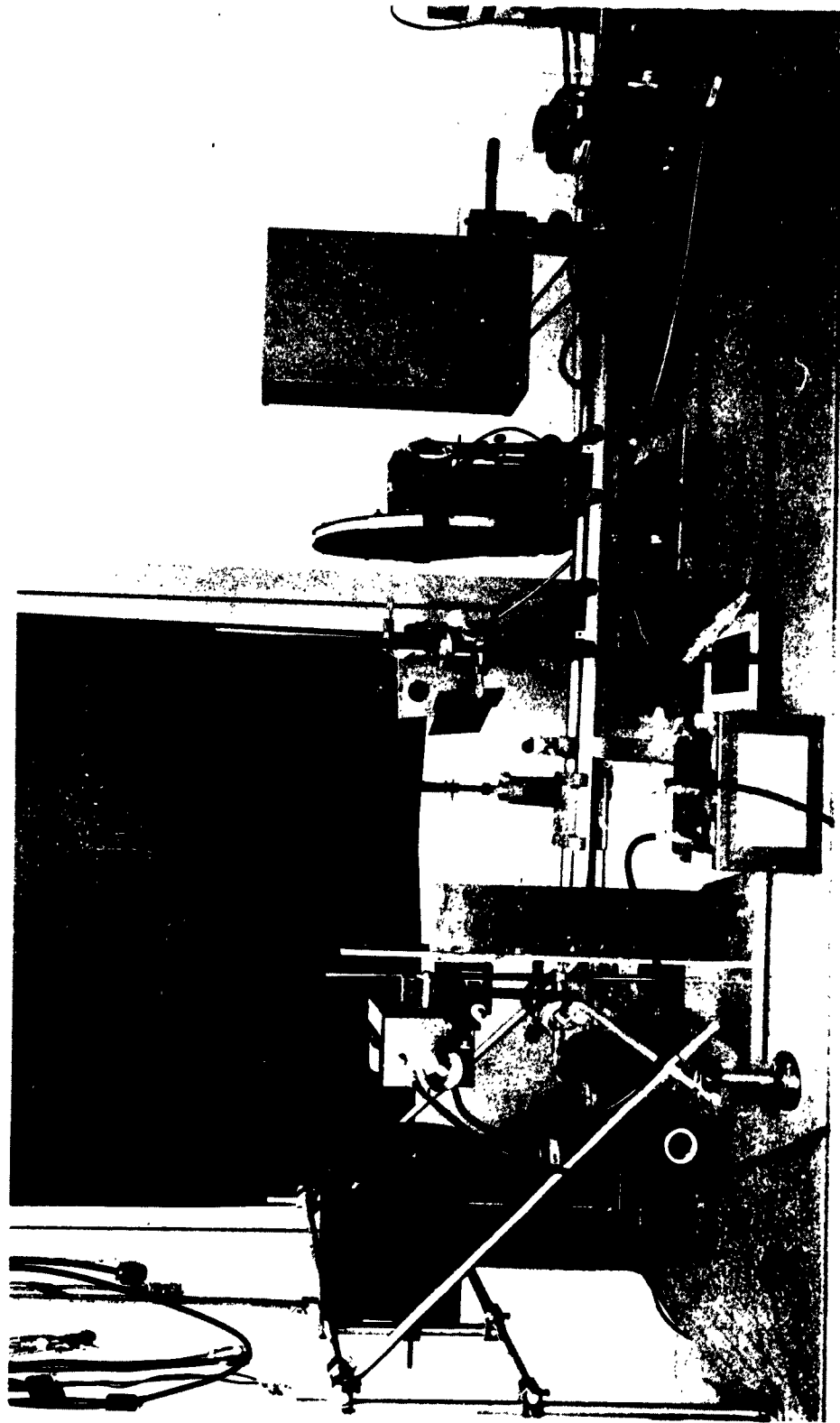


FIG. 3 OPTICAL BENCH ARRANGEMENT FOR OBSERVING PHOTOCONDUCTIVE  
RISE CURVES

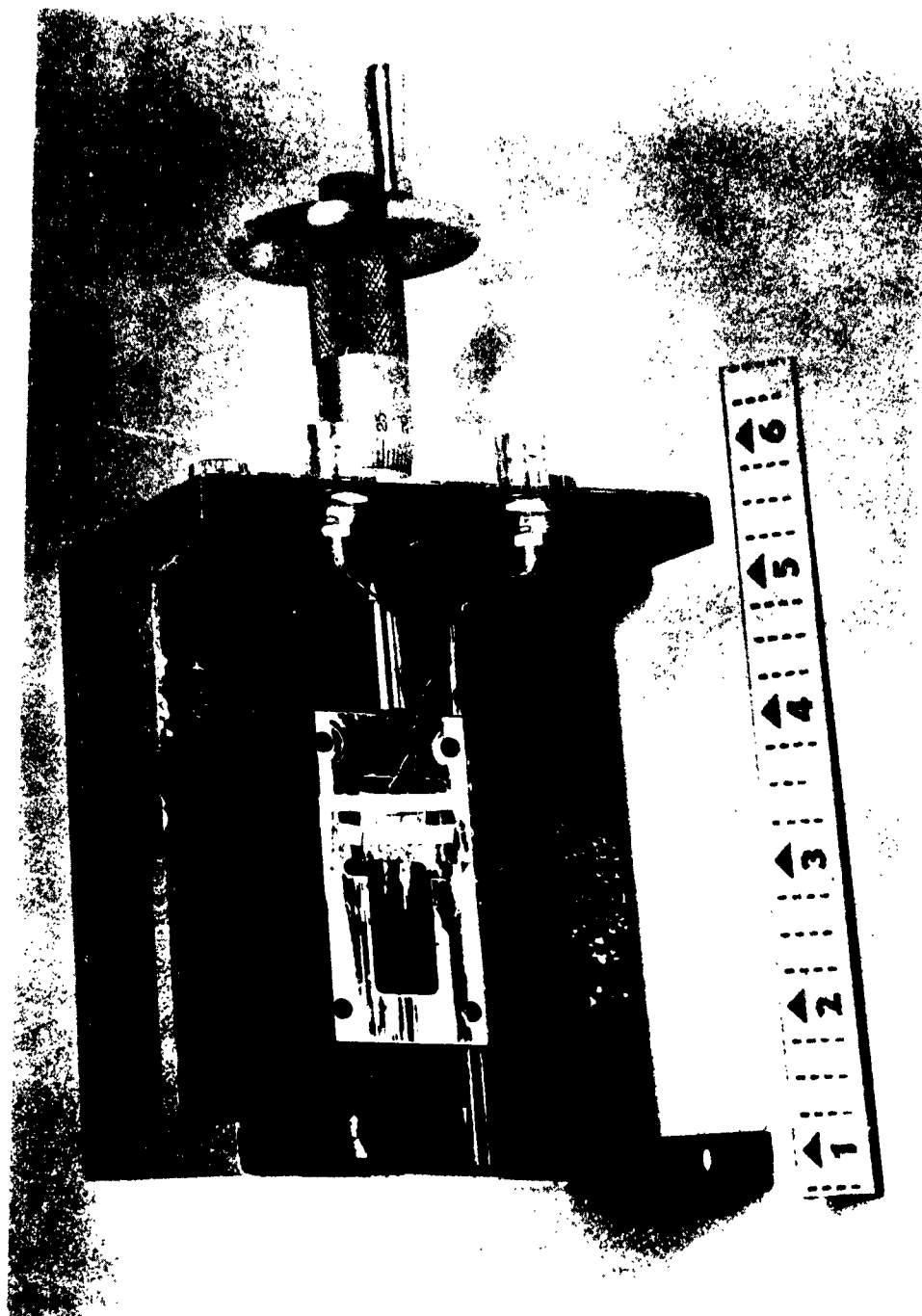


FIG. 4 SAMPLE HOLDER

true absorption in the region of the electrodes, (b) exciton diffusion from the illuminated region to the contact region where the excitons may be thermally ionized to yield free carriers, and (c) absorption and re-emission of luminescent radiation leading finally to generation of carriers by re-absorption in the electrode region.

If the photoconductivity is due to (a) above the photocurrent will initially increase with time according to

$$I = \int_0^T \alpha F dT \approx \alpha F T \quad (1)$$

where  $F$  is the photon flux incident on the crystal and  $\alpha$  is that fraction of the incident flux which is scattered and absorbed near the contacts. The multiplier  $\alpha$  will depend on the distance between the contacts and the incident light.

If exciton diffusion plays an important role in the long-range photoconductivity, we would expect the initial increase of the photocurrent to be described by

$$I = I(F) I(\beta) I(T) \quad (2)$$

where

$$I(T) \approx T (1 + e^{-T/\tau}) + 2\tau (e^{-T/\tau} - 1) \quad (3)$$

Eq. (2) assumes the photocurrent is separable into three factors. The first factor  $I(F)$  depends only on the incident light flux. The second factor,  $I(\beta)$ ,

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takes into account exciton generation efficiency and the probability that excitons reach the contact region, i. e.,  $I(\beta)$  depends on the exciton lifetime and diffusion coefficient. The third factor,  $I(T)$ , indicates the functional dependance on time of the rise of the photocurrent, but contains no amplitude information; the amplitude is given by the product  $I(F) I(\beta)$ .

The derivation of Eq. (3) is given in Appendix II of this report; this equation is plotted in Figure 5. It must be noted that the origin does not represent the beginning of the illumination pulse - rather it is the point experimentally determined to be the beginning of the photoconductive rise curve. The onset of photoconductivity will be delayed by the time it takes the excitons to diffuse from the illuminated region to the contact region.

The third possible mechanism, the absorption and re-emission of luminescent radiation, will exhibit a rise curve similar to that in Figure 5 (with the appropriate time constant), but there will be no delay between the beginning of the illumination pulse and the onset of photoconductivity.

Most of the 50 crystals of CdS examined for evidence of exciton transport showed only the linear rise of the photocurrent with time, suggesting that the observed currents were due to scattered light according to Eq. (1) or to luminescent re-radiation characterized by a very short lifetime. An example of this type of result is shown in Figure 6. The important feature of the curves in Figure 6 are; (a) the curves are essentially identical for all separations between the illuminated region and the contacts, and (b) the rise curves are linear. In all the work reported in this section the maximum photocurrents are independent of the separation between the illuminated region and the contacts; that is, in the case of linear curves the product  $\alpha F$  in Eq. (1) is constant. This is accomplished by adjusting the light intensity.

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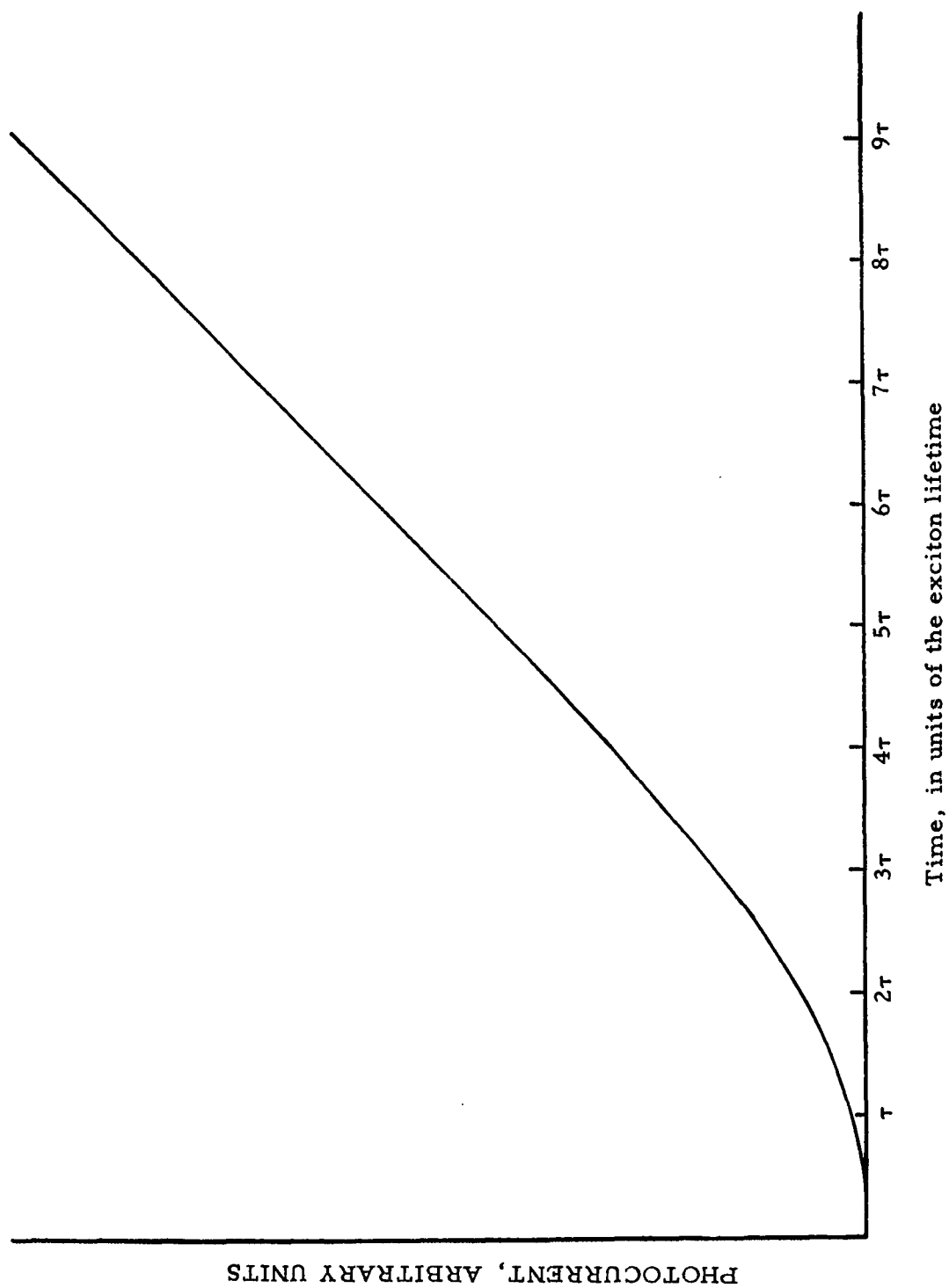


Fig. 5 - CALCULATED PHOTOCONDUCTIVITY RISE CURVE DUE TO EXCITONS

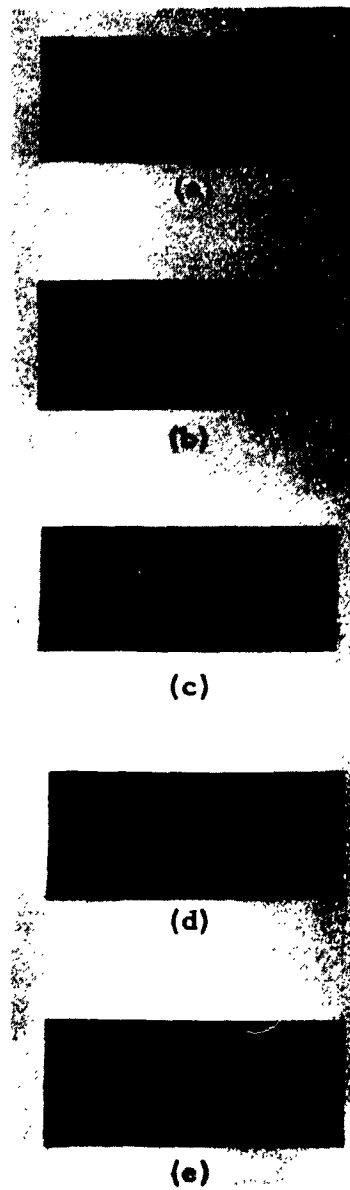


Fig. 6 - Photoconductive rise curves for sample A-22. In the series (a) through (e) the light spot is respectively 4mm, 3mm, 2mm, 1mm, and 1/2mm from the contacts. Time increases to the left, at the rate of 100 $\mu$  sec/div.

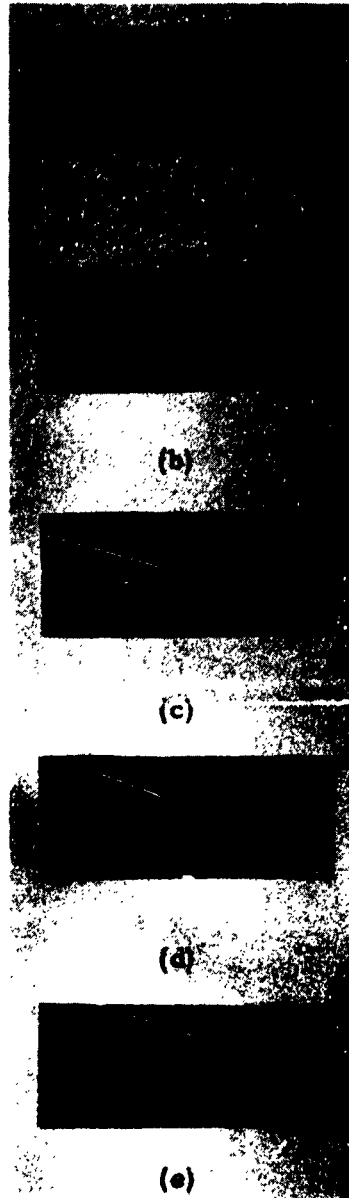


Fig. 7. - Photoconductive rise curves for sample A-13. In the series (a) through (e) the light spot is respectively 4mm, 3mm, 2mm, 1mm, and 1/2mm from the contacts. Time increases to the left, at 100 $\mu$  sec/div.

Such a procedure eliminates any non-linear saturation effects which are sometimes observed in CdS.

In contrast to the results in Figure 6 some crystals exhibited photoconductive rise curves such as are shown in Figure 7. Notice that when the illuminated region is farthest from the contacts the curve is linear, but as the illuminated region is moved closer to the contacts a marked departure from linearity occurs. Bearing in mind that this is not a saturation effect as discussed above, it is clear that there is another mechanism contributing to the photoconductivity, a mechanism which becomes more dominant as the light spot gets closer to the contacts. The disappointing feature is that the curves in Figure 7 bear little resemblance to the curve shape expected when excitons are important in the photoconductivity (Figure 5). We have not been able to explain satisfactorily why the slope of the rise curve should decrease after times of the order of  $100\mu$  sec. An hypothesis which does lead to the experimental curve shape is as follows. If the observed curve shape is actually due to two contributions, scattered light and exciton diffusion (which is quite likely), the observed curve shape can be obtained by allowing the exciton contribution to decay to zero after several lifetimes. This is merely an hypothesis, and considerable research will be required to investigate the plausibility of this hypothesis; this effort has been initiated. It should be noted that infrared radiation ( $8-12\mu$ ) has no apparent effect on the observed curve shapes.

It is known that the probability of exciton formation increases with decreasing temperature. In an attempt to exploit this behaviour seven crystals were examined at  $77^{\circ}\text{K}$ . The photoconductive rise curves were measured and high sensitivity dc measurements were made in the search for an effect

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on the photocurrent due to infrared. A general view of the experimental arrangement is shown in Figure 8.

The departure from non-linearity in the rise curves is generally more pronounced at 77°K, but yet the application of infrared to the sample caused no observable change in the photocurrent. The advantages in working at low temperatures when observing exciton behaviour are sufficient, however, that much future work will be done at 77°K in our efforts to rediscover exciton modulation of the photocurrent.

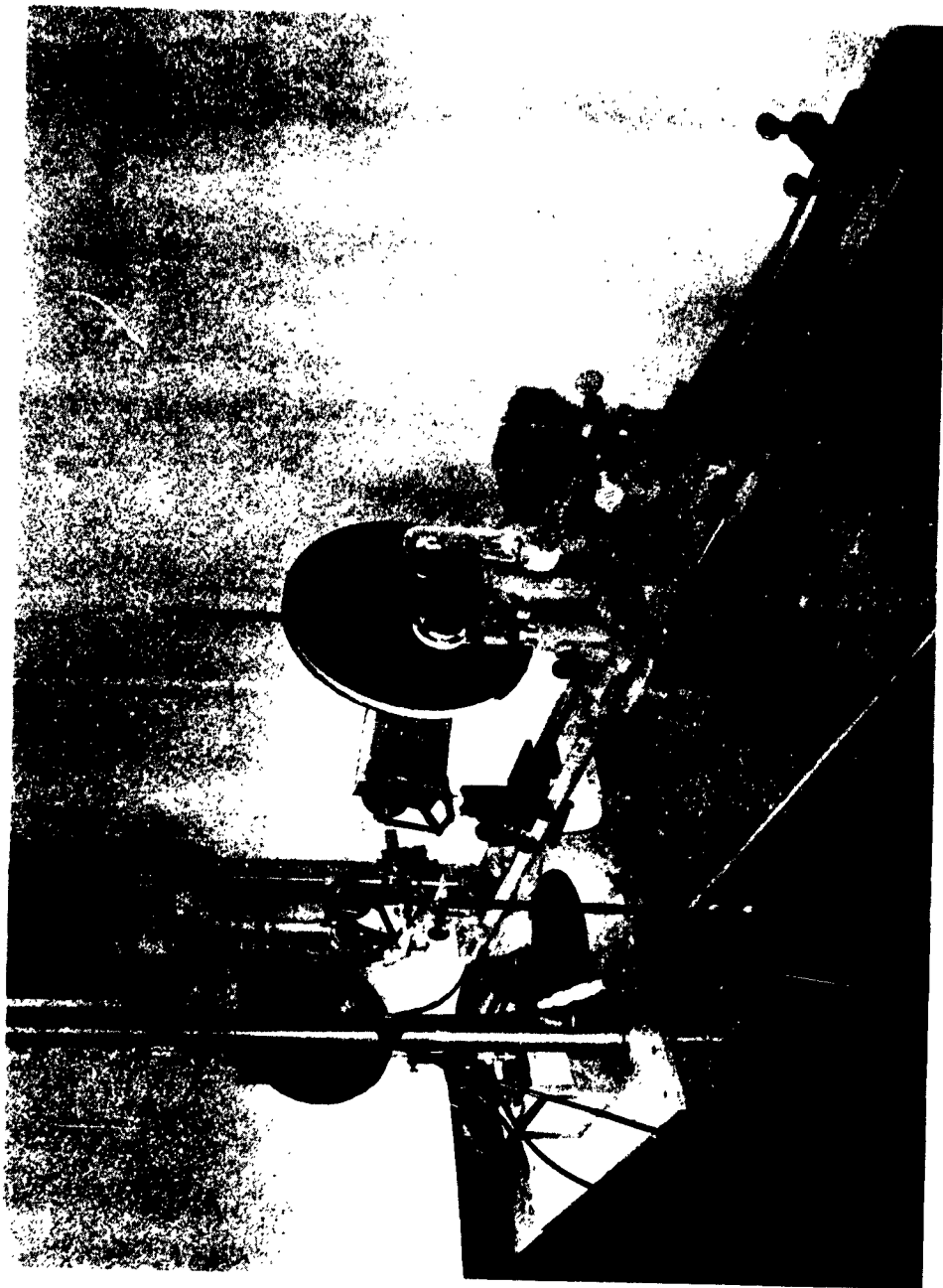


FIG. 8 OPTICAL BENCH ARRANGEMENT FOR OBSERVING PHOTOCONDUCTIVE  
RISE CURVES AT  $77^{\circ}\text{K}$ .

## APPENDIX II

### THE EXCITON CONTRIBUTION TO THE INCREASE OF THE PHOTOCONDUCTIVITY

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## APPENDIX II

### THE EXCITON CONTRIBUTION TO THE INCREASE OF THE PHOTOCONDUCTIVITY

In this Appendix we derive an expression for the initial shape of the photoconductive rise curve when the photoconductivity is due solely to excitons. Several assumptions are inherent in the derivation, but it is believed that the final result does not deviate greatly from an exact treatment. The exact treatment is impossible at this time, for there is not enough information available on exciton transport processes and decay mechanisms.

We assume that a portion of the crystal is illuminated with a light beam which is turned on at  $T = 0$ . Exciton generation, then, begins in the illuminated region at  $T = 0$  and these excitons (lifetime  $\tau$ ) diffuse randomly through the crystal. The density of excitons in the illuminated region will approach a steady state value exponentially according to  $(1 - e^{-T/\tau})$ , assuming monomolecular kinetics. The exciton density elsewhere in the crystal will have the same functional dependence on time, but the appearance of the first excitons elsewhere will occur some time after the light is turned on. Similarly, the exciton flux away from the illuminated region will have this same functional dependence with a retarded time. The last assertions assume that the diffusion velocity of excitons is concentration independent, which is quite likely to be the case for the exciton concentrations normally produced.

We assume an imaginary plane between the illuminated region and the contacts to the crystal such that all excitons which cross this plane eventually contribute to the photocurrent, while all other excitons make no

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contribution to the photocurrent. This imaginary plane will be of the order of one ambipolar diffusion length away from the contacts; this plane defines the "contact region."

We can write the flux density of excitons entering the contact region as  $N_0(1-e^{-T'/\tau})$  where  $T'$  is measured from the instant the first exciton enters the contact region and  $N_0$  will depend on the separation between the illuminated region and the contact region. Further, each exciton entering the contact region has a probability of ionization given by  $[1-e^{-(T''-T')/\tau}]$  where  $T'' - T'$  is the time that exciton has been in the contact region.

Consider a small group of excitons that entered the contact region in the time interval between  $T'$  and  $T' + \Delta T'$ , and we wish to know how many of these excitons have ionized at a later time  $T''$ . It follows from the above discussion that the number of excitons that have ionized at  $T''$  is (for unit cross-section area)

$$N_0 [1-e^{-T'/\tau}] [1-e^{-(T''-T')/\tau}] \Delta T'. \quad (1)$$

To arrive at the total number of all excitons that entered the contact region which have ionized at  $T''$  we simply integrate Eq. (1) between the limits  $T' = 0$  and  $T' = T''$ :

$$\begin{aligned} N &= N_0 \int_0^{T''} (1-e^{-T'/\tau}) (1-e^{-(T''-T')/\tau}) dT' \\ &= N_0 \left[ T'' (1 + e^{-T''/\tau}) + 2\tau (e^{-T''/\tau} - 1) \right]. \end{aligned}$$

Now we can substitute T for T'' and write the final result as

$$N = N_0 \left[ T (1 + e^{-T/\tau}) + 2\tau (e^{-T/\tau} - 1) \right]$$

where it must be remembered that T is measured from the instant the first exciton enters the contact region; experimentally, this is equivalent to measuring T from the beginning of the observed photoconductive rise curve.

## REFERENCES

1. G. Diemer, G. J. van Gurp and W. Hoogenstraaten, Philips Res. Repts. 13, 458 (1958) and 14, 11 (1959).
2. N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Oxford, p. 83.
3. D. G. Thomas and J. J. Hopfield, Phys. Rev. 116, 573 (1959).
4. R. J. Collins and D. A. Kleinman, to be published.
5. J. W. Allen, "Proceedings of the International Conference on Semiconductor Physics, Prague, 1960;" Publishing House of the Czechoslovak Academy of Sciences, Prague, 1961, p. 435.
6. J. O. Kessler and A. R. Moore, reference 5, p. 804.
7. M. Balkanski, reference 5, p. 839.
8. Bube, R. H., Phys. Rev. 99, 1105 (1955).